Evaluation of Amorphous Silicon as a Direct Water Splitting System

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Table of Contents

Abstract

Evaluation of Amorphous Silicon as a Direct Water Splitting System. KEN VARNER (University of North Carolina at Chapel Hill, Chapel Hill, NC 27514) JOHN TURNER (National Renewable Energy Laboratory, Golden, CO 80401-3393).

Analyses of amorphous silicon (a-Si) electrodes were performed with the goal of creating a monolithic water-splitting device. Tests included corrosion, current-voltage measurements, and metal-ion surface treatments. Results showed that amorphous silicon carbide (a-SiC) produced under three different conditions have a dissimilar performance. Also, the a-Si electrodes underwent surface treatments with two metal-ion solutions (Ru and Pt) and a porphyrin (Ru). All surface treatments decreased solar cell performance in the electrodes contradicting published results. Further work will be done on new samples with the metal-ion solutions as surface catalysts.

Research Category: Physics

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Introduction

As the world's population grows, causing a direct increase in energy consumption, the environment will experience a heavy burden. Consequently, there will be strong pressure to reduce CO_2 emissions, causing villages and entire countries to look for solutions in renewable energy and technologies. The solutions most likely to be considered are systems that contain effective energy storage. Energy storage is especially important for systems that use intermittent resources such as wind and photovoltaics (PV). The production of hydrogen through renewable energy systems will play a key role in attaining a sustainable energy infrastructure (Turner, 1999).

Hydrogen, produced directly from sunlight, can be stored and used as the chemical energy in transportation systems. Currently, PV systems are used to obtain hydrogen from water. PV panels use sunlight to supply the electrical energy to electrolyzers, which splits the water. Electrolyzers are commercially available but expensive. Our goal is to use photoelectrolysis as an advanced and less expensive alternative to the described system.

Photoelectrolysis systems work by using rays of sunlight that strike the surface of a semiconductor within a solution to split water directly on the surface. The primary advantage is that electrical cables and an electrolyzer are no longer needed. Combining a water splitting technique with a simplified PV system eliminates the high capital costs of a full-size hydrogen-producing PV system. A proposed system that will integrate this

new photoelectrolysis technology consists of structures containing water and photoelectric cells placed in rows on the bottom. The devices can be used with solar trackers in hydrogen-producing farms.

Two issues arise with amorphous silicon's ability to function as a suitable semiconductor for electrolysis: (1) Is the material's band gap sufficient enough to split water? (2) Is the material stable in aqueous electrolyte solution? Regarding the first issue, the theoretical voltage for splitting water to occur is 1.23 V. By adding overvoltages, an effective water splitting system must produce 1.6 V. State-of-the-art triple-junction a-Si semiconductors can have voltages greater than 1.8 V. The second issue may be addressed by applying a surface coating of amorphous silicon carbide (a-SiC) as a protective layer for the PV devices. Also, research shows that an application of transition metal-ions to the surface of the semiconductor allows electricity to transfer quickly to the water from the semiconductor and prevent surface corrosion (Bansal, et al., 2000; Allongue, et al., 1984; Kobayashi, et al., 1994).

This project's goal is to develop an a-Si-based system that will split water into hydrogen and oxygen through a-Si's direct surface contact with water. This system should split water upon illumination using only sunlight as the energy input. The a-Si samples were characterized to evaluate their potential for water-splitting. The various samples underwent current-voltage tests, corrosion measurements, and metal-ion catalyst treatments.

Materials and Methods

KOH and concentrated H_2SO_4 from J. T. Baker, dichloroethane (DCE) from Aldrich, and t-Octylphenoxypolyethoxyethanol (Triton X-100) from Sigma were used as received. The ruthenium octaethyl porphyrin (RuOEP) was manufactured by Midcentury. We made RuOEP to 15 mM in DCE. A 0.010 M $RuCl_3$ solution in 1.5 pH HCl was used from a previous study (Bansal, et al., 2000). We also used a .0077 M potassium hexachloroplatinate (K_2PtCl_6) solution.

Our materials included a-Si films (p-i-n solar cells) that were deposited on stainless steel substrates via plasma-enhanced chemical vapor deposition (PECVD) with a germane-to-disilane ratio of 0.72. This ratio is typically used for the i-layer in the bottom cell of the triple-junction cell. Some samples contain heavily doped a-SiC p-layers. These are deposited under the same conditions as a-Si films but their radio frequency (RF) power and deposition times vary with RF power values at 20 W, 50 W, and 160 W and their corresponding deposition times for the p-layer were 3.0 min, 2.5 min, and 1.5 min. Each sample was made into a 2" by 2" wafer, which was then cut into small pieces (0.02 cm^2 – 2.2 cm^2). We attached each piece to a copper wire with electrically conductive silver epoxy and then placed it in an oven for over an hour at 80°C. After curing the Ag epoxy, we covered the side and the back of the electrode with a non-conductive epoxy so that only the a-Si's surface (.02-.21 cm^2) was exposed to the solution. Some of the samples were chemically modified using three techniques: metal-ion dip-coating, porphyrin drop evaporation, and photoelectrochemical plating.

In the metal-ion dip-coating application, we immersed electrodes in the RuCl$_3$ for 60 seconds. We then rinsed the electrode with distilled water, and dried the surface by blowing nitrogen gas across the surface.

We performed the porphyrin drop evaporation method by placing a 50 µL drop of the 15 mM RuOEP solution on the electrode's surface. The porphyrin dried after 60 seconds and the electrode was rinsed with distilled water.

The photoelectrochemical plating technique used an electrode connected in a circuit with a platinum (Pt) flag (3.75 cm^2) submerged in .0077 M K$_2$PtCl$_6$ solution. We irradiated 80 mW/cm^2 of light with a Cole-Parmer 41500-50 Fiber Optic Illuminator housing a 50 W halogen bulb on the a-Si electrode for 15 seconds. The electrode was then rinsed with distilled water and dried with nitrogen.

We performed corrosion measurements in a three-electrode cell with an a-Si electrode, the Pt flag mentioned above as the counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode all in solution. Current-voltage (I-V) measurements were performed in a two-electrode setup. This consisted of the a-Si semiconductor electrode and the Ag/AgCl reference electrode. In both setups, the a-Si electrode was illuminated with the fiber optic illuminator. We conducted the corrosion tests on a Voltalab PGZ 301 potentiostat in 1 M KOH and 1 M H$_2$SO$_4$ solutions under 210 mW/cm^2 light on the semiconductor's surface. We applied a bias potential of –500 mV and ran the experiments for 3600 seconds. Each sample tested had been metal-ion dip-coated with

RuCl$_3$. The I-V measurements were conducted on a Solartron 1287 Electrochemical Interface and a Solartron 1260 Impedance/Gain-Phase Analyzer. We used CorrWare 2 and CorrView to collect and analyze the I-V data measurements. The experiments were conducted in 1 M H$_2$SO$_4$ solution with 210 mW/cm^2 of light impinging the electrode's surface. The scan rate was 10 mV/s and measurements were made at 500 Hz with a 5 mV rms amplitude.

Results

Figure 1 shows corrosion measurements for three samples containing a-SiC on the top surface. The triple junctions underneath the a-SiC top layer are the same for each sample. The measurements occurred in 1 M KOH and each sample was RuCl$_3$ dip-coated before testing. Under the same conditions, each sample functioned differently, especially sample L3524-1 which had a dramatically lower performance than the other two samples. The graph also shows that corrosion occurs within the hour for samples L3524-2 and L3524-4.

Graph 2 shows corrosion measurements for the three samples mentioned above except in 1 M H$_2$SO$_4$ solution. The graph displays L3524-1's lower performance as compared to the other two samples.

Displayed in Graph 3, Graph 4, and Graph 5 are I-V measurements for samples L3524-2, L3524-4, and L3586-4, respectively, and the effects of $RuCl_3$, Pt, and RuOEP treatment on each sample. A control, non-treated sample was also measured for each set.

Discussion and Conclusion

Corrosion is one of the key problems that needs to be overcome in our a-Si water-splitting systems. Previous experiments showed that a-SiC as a top layer does provide corrosion protection (Varner, 2001). In our experiments, we tested to see how different a-SiC layers on the top surface individually affected the system's performance. Graph 1 and Graph 2 show that different production parameters for the a-SiC do change the triple junction's current density. Sample L3524-1 had a considerably lower current density in 1 M KOH solution than in 1 M H_2SO_4. Consistently, we were unsuccessful in measuring L3524-1's a-SiC layer's band gap while we did obtain a value for L3524-2 and L3524-4's a-SiC's band gaps (Varner, 2001). Whether or not L3524-1's lacking band gap caused the dramatic performance difference in acid and base, we do not know. Further study must be done.

Samples L3524-2 and L3524-4's current densities were about the same in both experiments. In 1 M H_2SO_4, L3524-2 displayed less corrosion over time when compared to its corrosion in 1 M KOH. Furthermore, Graph 1 and Graph 2 both show that L3524-2 has a more negative current density than the other samples. We can conclude that

different production parameters for the a-SiC layer do change triple junction performance.

In the metal-ion surface treatment experiments, we expected the $RuCl_3$ and Pt surface treatments to shift the I-V curves in a positive voltage direction (Bansal et al., 2000). By shifting the curves positive, current density and hydrogen production increase. However, Graph 3, Graph 4, and Graph 5 show that the metal-ions shifted the curves in the negative direction. The untreated electrodes displayed the highest current density in each graph.

Graph 6 displays L3524-2, L3524-4, L3586-4 without any metal-ion or porphyrin surface treatment. By taking the current density value at 0 V and using Equation 1, one

$$\text{Efficiency} \; = \; \frac{J \times E^0}{\text{Irradiance (W/cm}^2)} \qquad\qquad (1)$$

can obtain the device's solar to hydrogen efficiency. J is the sample's current density in A/cm^2 and E^0 stands for the water splitting reduction potential (1.23V). From Graph 6 one calculates L3524-2's, L3524-4's, and L3586-4's solar-to-hydrogen efficiencies at .13%, .26%, and .41%. We conclude that L3524-2 and L3524-4 display a lower efficiency because of the a-SiC surface layer (Varner).

Acknowledgements

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Figure 1

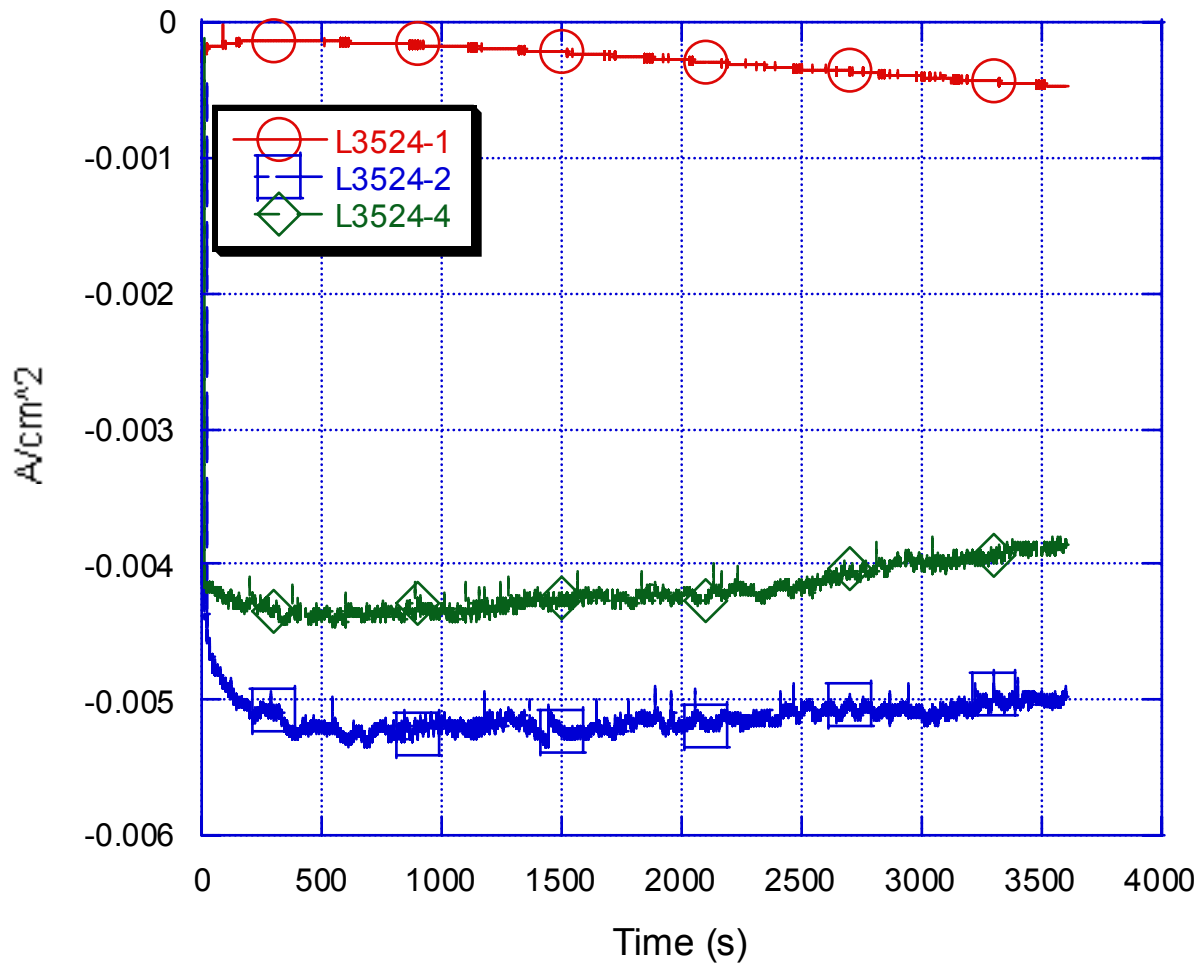# L3524 with Different a-SiC
Top Layers in 1 M KOH

Figure 2

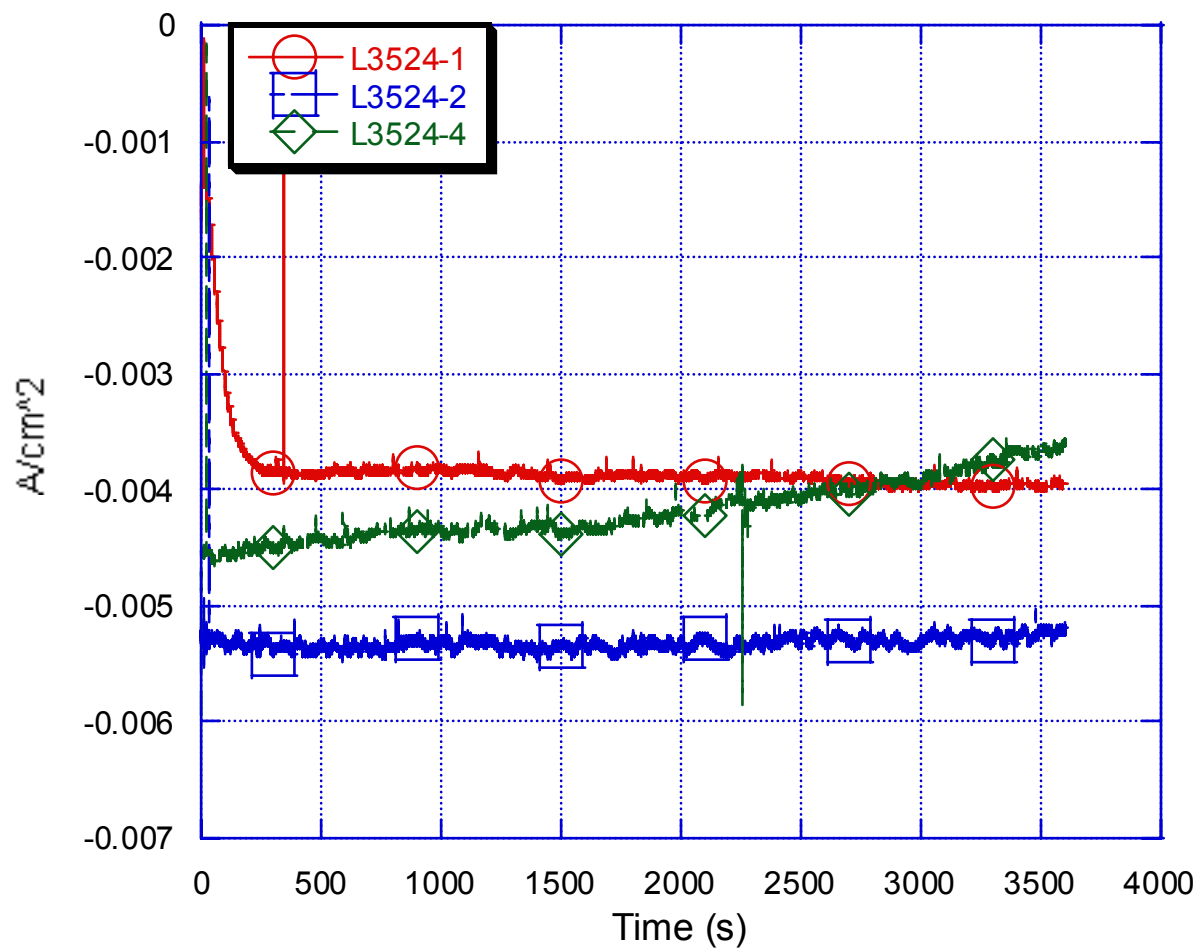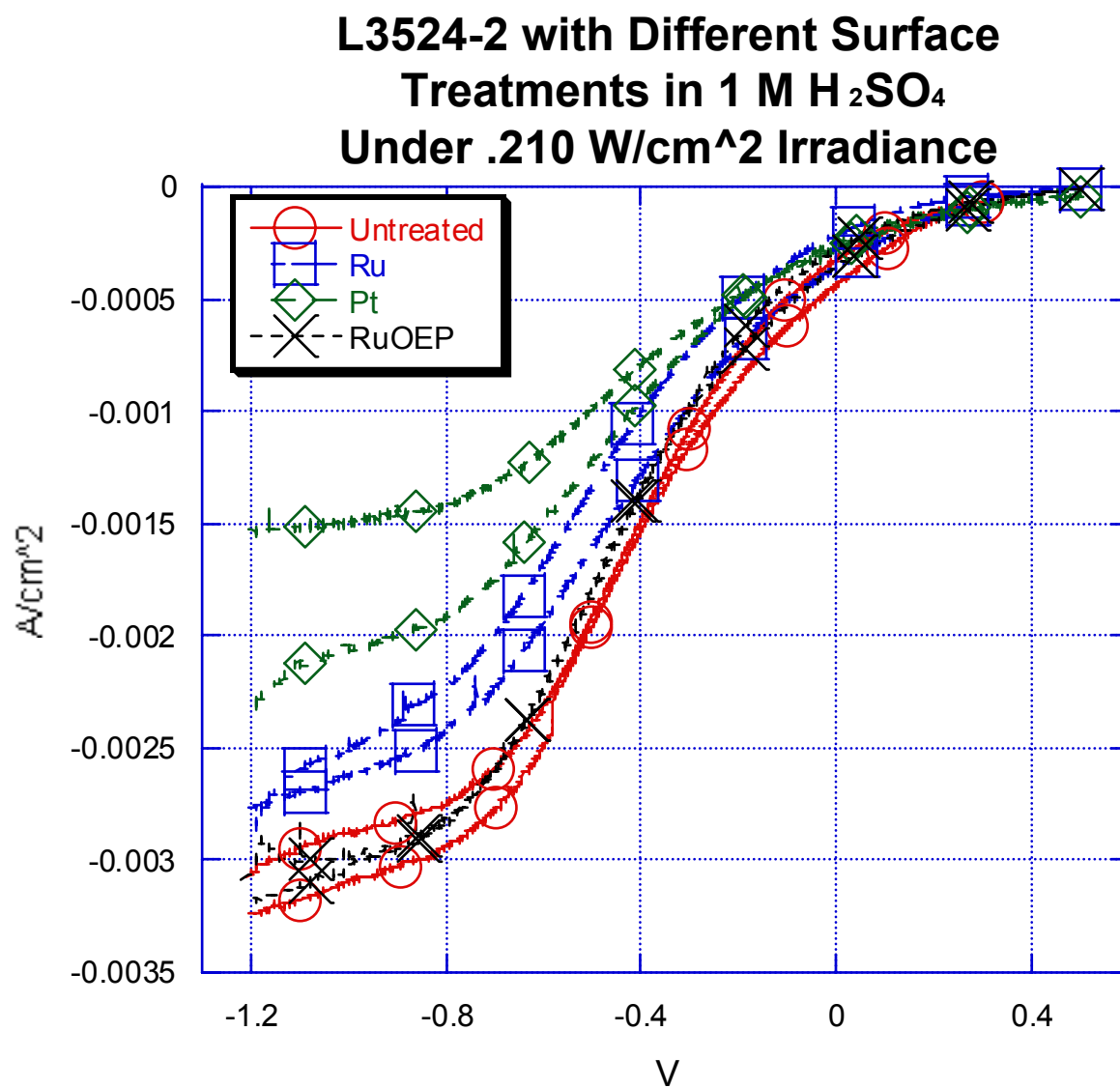# L3524 with Different a-SiC
Top Layers in 1 M H$_2$SO$_4$

Figure 3

L3524-2 with Different Surface Treatments in 1 M H$_2$SO$_4$ Under .210 W/cm^2 Irradiance

Figure 4

L3524-4 with Different Surface Treatments in 1 M H$_2$SO$_4$ Under .210 W/cm^2 Irradiance

Figure 5

L3586-4 with Different Surface Treatments in I M H₂SO₄ Under .210 W/cm^2 Irradiance

Figure 6

Comparison of Three Samples
with Different Surface Layers
in 1 M H_2SO_4 and .210 W/cm^2